

Report No. IITRI-U6002-36
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

George C. Marshall Space Flight Center
National Aeronautics & Space Administration
Huntsville, Alabama

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DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

Contract No. NAS8-5379
IITRI Project U6002

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February 21, 1966

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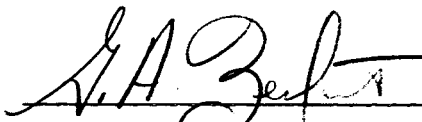
FOREWORD

This is Report No. IITRI-U6002-36 (Triannual Report) of IITRI Project U6002, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." The report covers the period from September 20, 1965 through January 20, 1966. Previous Triannual Reports were issued on October 25, 1963, March 5, 1964, July 20, 1964, December 21, 1964, February 23, 1965, July 20, 1965 and November 9, 1965.

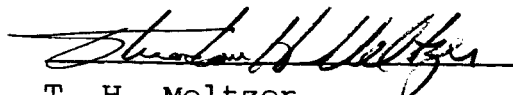
Major contributors to the program during this period include Gene A. Zerlaut, Project Leader; John E. Gilligan, general consultation; Dr. G. A. Rubin and William R. Logan, inorganic coatings and pigment studies; Douglas G. Vance, reflectance measurements and space simulation tests; Noel D. Bennett, silicone paint preparation and reflectance measurements; and Wayne Ridenour and W. C. Courtney, design of space chamber with in situ reflectance-measurement capability. Dr. T. H. Meltzer, Manager of Polymer Research, provided administrative supervision. The work reported herein was performed under the technical direction of the Research Projects Laboratory of the George C. Marshall Space Flight Center with Daniel W. Gates acting as Project Manager.

Data are recorded in IITRI Logbooks C13423, C13736, C13802 and C14176.

Respectfully submitted,
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ABSTRACT

Pigment screening studies during this report period have shown the excellent stability of double zirconium silicates, especially those of magnesium and calcium. Although its initial solar absorptance was high, a compacted forsterite powder exhibited a $\Delta\alpha$ of only 0.015 in 2000 ESH. Also of significance was the stability exhibited by a zinc titanate-pigmented potassium silicate paint; a $\Delta\alpha$ of 0.03 in 2000 ESH with an initial α of only 0.09 was observed. Additional studies of Alucer MC α -alumina have confirmed the observed instability of earlier experiments.

The anomalous degradation of zinc oxide and zinc oxide-pigmented silicone paints investigated. This phenomenon, which is not exhibited by zinc oxide-pigmented potassium silicate coatings (Z93), results in severe reflectance losses in the infrared spectrum which are observable only when the measurements are performed in situ. The absorption is believed to be due to photodesorption of oxygen on the surface of the zinc oxide, resulting in the generation of high concentrations of free carriers. The process occurs immediately upon irradiation in vacuum; the defects are instantaneously "bleached" when air and nitrogen, but not argon, are admitted to the space simulation chamber. Analysis of these data suggested that a potassium silicate-treatment of zinc oxide might preclude the photodesorption process.

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Such treatments were successful; potassium silicate-treated SP500 zinc oxide does not exhibit the free carrier absorption when irradiated in vacuum, either as a powder or as an S-13-type paint.

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

The general requirement under this contract is for development of thermal-control surface coatings with a very low but stable ratio of solar absorptance (α) to infrared emittance (ϵ_H). The work is currently proceeding in two major directions: (1) studies of inorganic pigments and (2) ultraviolet photolysis studies of methyl silicone polymers.

The studies of inorganic pigments involve screening and evaluation of materials parameters that affect pigment stability. These studies are aimed at finding or preparing stable pigments that are potentially useful in formulating coatings with a very low solar absorptance. Emphasis has been placed on the preparation parameters affecting degradation.

The ultraviolet photolysis of methyl silicone polymers involve electron spin resonance and mass spectrometry investigations of carefully prepared methyl and methyl-aromatic silicones irradiated in a vacuum. Work during this report period has involved the construction of an improved ultraviolet-irradiation facility for use with IITRI's Hitachi RMU-6D high-resolution mass spectrometer.

Secondary efforts during this report period involved (1) an investigation of the infrared anomaly exhibited by zinc oxide and zinc oxide-pigmented silicones in vacuum, (2) the design of a space simulation facility possessing a capability for making

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in situ hemispherical spectral reflectance measurements, and
(3) general space-simulation tests on zinc oxide-pigmented
silicones and potentially useful polymers.

II. PIGMENTS AND INORGANIC COATINGS

A. Introduction

Work during this period included (1) continuation of pigment screening tests, (2) study of the effect of calcination of pigments and paints on their ultraviolet-stability, and (3) initiation of a theoretical approach to explain possible changes of the defect structure of oxide pigments under ultraviolet-irradiation in vacuum which may lead to an increase in solar absorption. It is expected that such a concept, developed on the basis of data accumulated here and elsewhere and with the aid of some critical experiments, will provide a more efficient pigment screening than possible to date. A more efficient screening procedure appears mandatory insofar as it has been found that a completely valid pigment evaluation requires in situ reflectance measurements.

B. Pigment Screening Tests

Space simulation tests were conducted on the following pigments: SnO_2 , MoO_3 , Ta_2O_3 , Al_2O_3 , ZnZrSiO_5 , CaZrSiO_5 , BaZrSiO_5 , MgZrSiO_5 , MgSiO_3 , and $2\text{MgO} \cdot \text{SiO}_2$. These materials were compacted under 50-60 psi in the "as-received" state and the reflectance was measured before and after exposure to simulated solar radiation. The exposure time was at least 500 ESH and was increased to 2000 ESH for the more promising samples. The latter were also tested as paints (PS7 potassium silicate binder) and the effect of different calcination treatments of pigment and paint

on the ultraviolet-stability was studied. The results are presented in Table 1, (Tests V70, V71, V73, and V74). In addition, experiments were initiated to study the effect of aging of SP-500 zinc oxide on its ultraviolet-stability and to investigate the optical properties of SP-500 zinc oxide newly developed by the New Jersey Zinc Company.

The significant results of this work are as follows:

(1) The zirconium silicates exhibited surprisingly good ultraviolet-stabilities. This is shown more clearly in Table 2. There appears to be no general trend insofar as the effect of calcination of the paint on the ultraviolet-stability is concerned. In the case of the magnesium zirconium silicate, the calcination definitely improved the ultraviolet-stability. These studies are currently being completed by investigating the effects of pigment calcination on their ultraviolet-stability and also by in situ reflectance measurements.

(2) Fused Forsterite $2\text{MgO} \cdot \text{SiO}_2$ showed a very low $\Delta\alpha$ of .015 after exposure to 2000 ESH. Its initial α of .242, however, is rather high.

C. Effect of Calcination on Ultraviolet-Stability of Aluminum Oxide Pigment

Alucer MC α -aluminum oxide pigment powders were calcined at 1000°C and 1620°C in air for 1 hour. The as-received and calcined powders were compacted under 50-60 psi and the solar reflectance was measured before and after exposure to 500 ESH. The results are listed in Tables 3 and 4. In Table 4, α -values for

Table 1

EFFECT OF HEAT TREATMENT ON UV-IRRADIATION INDUCED DEGRADATION
OF PIGMENTS AS POWDER COMPACTS AND WITH BINDER PS7
(TEST 73 AND 74)

Specimen	Material	Treatment	Binder	Exposure ESH	Solar Absorbance		
					μ_1	μ_2	$\Delta \mu_s$
7208	ZnTiO ₃ (TAM)	As received	-	0 1000	.077 .126	.034 .065	.111 .191 .080
7210	ZnTiO ₃ (NJZ)	As received	-	0 1000	.092 .116	.055 .076	.147 .192 .045
7221	ZnTiO ₃ (NJZ)	As received	PS7	0 2000	.052 .078	.041 .039	.093 .117 .024
7220	ZnTiO ₃ (NJZ)	As received Paint 500°C/ 1 hr	PS7	0 0 2000	.054 .053 .081	.039 .040 .041	.093 .093 .122 .029
7194	ZnZrSiO ₅	As received	-	0 2000	.078 .132	.045 .049	.123 .181 .058
7212	ZnZrSiO ₅	As received	PS7	0 1000	.071 .169	.083 .082	.154 .251 .097
7224	ZnZrSiO ₅	As received Paint 500°C/ 1 hr	PS7	0 0 2000	.104 .122 .154	.087 .090 .090	.191 .212 .244 .032
7195	CaZrSiO ₅	As received	-	0 2000	.083 .120	.032 .039	.115 .159 .044
7215	CaZrSiO ₅	As received	PS7	0 1000	.093 .111	.072 .066	.165 .177 .012

Table 1 (continued)

Specimen	Material	Treatment	Binder	Exposure* ESH	Solar Absorptance		
					α_1	α_2	$\Delta \alpha_s$
7225	CaZrSiO ₅	As received Paint 500°C/ 1 hr	PS7	0 0 2000	.103 .113 .134	.075 .065 .065	.178 .178 .199 .021
7197	MgZrSiO ₅	As received	-	0 2000	.072 .123	.030 .037	.102 .160 .058
7217	MgZrSiO ₅	As received	PS7	0 1000	.075 .145	.063 .060	.138 .205 .067
7226	MgZrSiO ₅	As received Paint 500°C/ 1 hr	PS7	0 0 2000	.093 .090 .121	.063 .055 .056	.156 .145 .177 .032
7222	Ta ₂ O ₅	As received Paint 500°C 1 hr	PS7	0 0 2000	.109 .108 .141	.103 .087 .095	.212 .195 .236 .041
7219	ZrO ₂	Sample Std.	PS7	0 2000	.074 .161	.077 .076	.151 .237 .086
7196	BaZrSiO ₅	As received	-	0 2000	.122 .215	.039 .058	.161 .273 .112
7198	2MgO·SiO ₂ Enstatite	As received	-	0 2000	.100 .222	.093 .106	.193 .328 .135
7199	2MgO·SiO ₂ Forsterite	As received	-	0 2000	.170 .179	.057 .063	.227 .242 .015

* Solar Factor = 5X

Table 2

ULTRAVIOLET-INDUCED DEGRADATION OF DOUBLE ZIRCONIUM
SILICATE POWERS AND PS-7 PAINTS (ABSTRACTED FROM TABLE 1)

<u>Material</u>	<u>Treatment</u>	<u>Exposure ESH</u>	<u>α_s</u>	<u>$\Delta \alpha_s$</u>
ZnZrSiO ₅	As received	-	.123	-
	As received	2000	.181	.058
	Paint	1000	.251	.097
	Paint Calc.	2000	.244	.032
	500°C/1 hr			
CaZrSiO ₅	As received	-	.115	-
	As received	2000	.159	.044
	Paint	1000	.177	.012
	Paint Calc.	2000	.199	.021
	500°C/1 hr			
MgZrSiO ₅	As received	-	.102	-
	As received	2000	.160	.058
	Paint	1000	.205	.067
	Paint Calc.	2000	.177	.032
	500°C/1 hr			

Table 3

EFFECT OF CALCINATION ON UV-IRRADIATION
INDUCED DEGRADATION OF COMPACTED %) (50 PSI)
α-Al₂O₃ PIGMENT POWDERS (TEST 72)

Specimen	Material	Treatment	Exposure ESH	Solar Absorptance		
				a ₁	a ₂	Δa _s
7202	Al ₂ O ₃ Alucel MC	As received	0	.038	.025	.063
			500	.122	.031	.153 .090
7206	Al ₂ O ₃ Alucel MC	Calcined 1000°C/1 hr	0	.037	.023	.060
			500	.118	.031	.149 .089
7207	Al ₂ O ₃ Alucel MC	Calcined 1000°C/1 hr	0	.019	.017	.036
			500	.113	.032	.145 .109
7203	Al ₂ O ₃ Alucel MC	Calcined 1620°C/1 hr	0	.024	.008	.032
			500	.128	.021	.149 .117
7204	Al ₂ O ₃ Alucel MC	Calcined 1620°C/1 hr	0	.021	.007	.029
			500	.119	.019	.138 .110
7205	ZrO ₂ PS7 Binder Sample Standard		0	.074	.079	.153
			500	.121	.096	.17 .064

Table 4

BRIEF REPRESENTATION OF RESULTS LISTED IN TABLE 3

Material	Before Irradiation			After Irradiation			
	u_1	u_2	u_T	u_1	u_2	u_T	Δu_T
Al ₂ O ₃ , Alucer MC-u							
As received	.038	.025	.063	.122	.031	.153	.090
Calcined 1000°C/1 hr	.028	.020	.048	.115	.032	.147	.099
Calcined 1620°C/1 hr	.022	.008	.031	.124	.020	.143	.113

samples of identical heat treatment and preparation, which are listed separately in Table 3, were averaged. It appears as if $\Delta\alpha$ increases with increasing calcination temperature, while the initial α decreases. It is possible, however, that the heat treatment changes the compacting characteristics of the Al_2O_3 powder.

A recent study of titanate powders (ref. 1) showed a considerable strain induced d-spacing shift and x-ray diffraction line broadening after compacting or milling of the powder. It is also conceivable that the powder particles sintered together to some small extent upon heat treatment, an effect which is observed macroscopically and described by the "sticking together" of rather large powder agglomerates.

In compacting the powder for reflectance measurements such weak bonds may break which results in "fresh" crystallite surfaces which, we have reason to believe, would strongly absorb gases. This negative effect may then overshadow any positive effect due to a higher degree of crystallinity of the crystallite surfaces which is expected to result from the heat treatment. An experiment is under preparation which will exclude the described uncertainty: the preparation of paints from heat-treated pigment powders whereby the powder particles experience none or negligibly small mechanical stresses and are separated from one another when already covered by the silicate solution.

D. Theoretical Approach

The optical properties of pigment powders depend to a large degree on the surface characteristics of the crystallites of the powder which may considerably deviate from the bulk properties of the same material. The surface structure of the crystallites is always a defect structure because the periodicity of the lattice is interrupted at the surface and the surface ions or atoms have to arrange themselves into a minimum free energy configuration under different conditions than the ions or atoms within the crystallite. Since the absorption of foreign atoms at the crystallite surface is normally an exothermic process, thus decreasing the surface free energy, the pigment crystallites usually carry an absorption layer the nature of which depends on thermal history, environmental conditions, and surface reaction kinetics. Ultraviolet-irradiation and changes of the oxygen partial pressure represent two of several means to alter the surface state of oxide pigment powders independently. Space simulation tests on pigment compacts or paints involve ultraviolet-irradiation and oxygen partial pressure changes simultaneously and part of the difficulty of interpreting the experimental results consists in the separation of possible contributions of the two effects to the total change in solar absorptance.

In our theoretical study, we try to combine a model mechanism for oxygen-partial-pressure-induced surface defects with a model for possible ultraviolet-irradiation defects in zinc oxide,

and similar materials such as TiO_2 , ZnS , SnO_2 which have already been studied extensively. A recent investigation of the relation between optical absorption and reduction kinetics of rutile (ref. 2) has shown that the vacuum reduction kinetics of TiO_2 produces a broad absorption band in the infrared region of the spectrum, around 1.2 micron, different from the band produced by hydrogen reduction which centers at 1.65 micron. The growth kinetics of the 1.2 micron peak can be associated with the self-diffusion of titanium in rutile. Field-induced diffusion of zinc interstitial ions in zinc oxide has been shown to be likely even at room temperature (ref. 3) and a similar mechanism may apply to the reduction-induced infrared absorption in zinc oxide. There also seem to be similarities between TiO_2 and ZnO with respect to F' centers and the broadening of F' bands with deviation from stoichiometry.

Future plans include:

- (1) Establishing the heat treatment conditions for calcium-, magnesium-, and zinc-zirconium silicate pigments which result in minimum α and $\Delta\alpha$ paints
- (2) Studying the ultraviolet-stability of SP-500 zinc oxide newly developed by the New Jersey Zinc Company
- (3) Theoretical study of the ultraviolet-irradiation and vacuum induced changes of the visible and infrared absorption in pigment compounds of current interest.
- (4) Conduction of space simulation tests including in situ reflectance measurements on pigments which appear promising on the basis of the theoretical studies.

III. METHYL SILICONE PAINTS AND MISCELLANEOUS SPECIMENS

The results of test Q-17, performed in the Quad-Ion space-simulation facility, are presented in Table 5. Specimen 5191B was prepared from Owens-Illinois Type 650 glass resin pigmented with Alucer MC α -alumina. Similar coatings exhibited solar absorptance increases of 0.03 and 0.06 in two previous tests. The solar absorptance increase of 0.062 exhibited by this coating in test Q-17 is in very close agreement with the degradation reported in test Q-16 (see p. 13, Triannual Report No. IITRI-U6002-31).

Similarly, specimens of "dry" and "wet" S-13 were irradiated in test Q-17 and the results were similar to those reported in the last Triannual Report (IITRI-U6002-31). The degradation for both S-13 specimens was more severe in the current test; the former test was for only 1700 ESH, however. The methods of preparation of the "dry" and "wet" specimens were described in the last Triannual Report.

Specimens 5201, 5202 and 5203 were prepared from pigments prepared by Lexington Laboratories, Inc. under contract* to the George C. Marshall Space Flight Center. Specimen 5201 was formulated from zinc oxide which has been prepared from zinc hydroxide. Specimens 5202 and 5203 were prepared from α -alumina; the pigment used in 5203 possessed chromium contamination.

Specimen 5203 was an SP500 zinc oxide-pigmented poly(methyl)-methacrylate prepared at 85% PVC. The material was somewhat

* Contract No. NAS3-20162

Table 5

EFFECT OF UV IRRADIATION IN VACUUM ON MISCELLANEOUS
WHITE PAINTS (Q-17)

Specimen	Remarks	Solar Factor	Exposure ESH	Solar Absorptance		
				a_1	a_2	Δa
5191B	Alucer MC α -Al ₂ O ₃ / Owens-Illinois 650	0 3	0 2000	.029 .080	.057 .067	.086 .147 .061
5192B	S-13 (Dry)	0 3	0 2000	.087 .098	.069 .080	.156 .177 .021
5193B	S-13 (Wet)	0 3	0 2000	.090 .107	.095 .104	.185 .211 .026
5201*	ZnO/Owens Illinois 650	0 3	0 2000	.151 .161	.128 .185	.279 .346 .067
5202*	α -Al ₂ O ₃ (light)/Owens Illinois 650	0 3	0 2000	.288 .450	.249 .332	.537 .782 .245
5203*	α -Al ₂ O ₃ (dark)/Owens Illinois 650	0 3	0 2000	.271 .427	.304 .339	.575 .766 .191
5204	SP500/poly(methyl) methacrylate 85% PVC	0 3	0 2000	.079 .090	.023 .033	.102 .123 .021
5205	Alucer MC α -Al ₂ O ₃ / RTV 602	0 3	0 2000	.042 .191	.059 .082	.101 .273 .172
5206	Alucer MC α -Al ₂ O ₃ / RTV 602	0 3	0 2000	.038 .200	.052 .074	.100 .274 .174

Table 5 (cont.)

Specimen	Remarks	Solar Factor	Exposure ESH	Solar Absorptance			
				α_1	α_2	α_s	$\Delta \alpha$
5207	PlasChem Coating (as received)	0 3	0 2000	.152 .279	.106 .131	.258 .410	.152
5208	PlasChem Coating (cleaned with Alconox)	0 3	0 2000	.139 .227	.100 .114	.239 .341	102
5211	Zirconia/PS7 PBR = 6.4	0 3	0 2000	.079 .171	.104 .107	.183 .278	.095
5212	Zirconia/PS7 PBR = 6.4	0 3	0 2000	.079 .170	.106 .110	.185 .280	.095

* The ZnO and α -Al₂O₃ pigments used in 5201, 5202 and 5203 were obtained from Lexington Laboratories, Cambridge, Mass., Contract NAS8-20162.

fragile and soft, but exhibited better film properties than would be indicated by such a high pigment volume concentration. The solar absorptance was only 0.10 and the increase on irradiation was only 0.02. This system will be examined further, although we expect the degradation to greatly increase as the pigment volume concentration is lowered.

Alucer MC α -alumina was used to pigment RTV-602. The resultant paints exhibited more than twice the increase in solar absorptance exhibited by Owens-Illinois Type 650 α -alumina-pigmented paints.

Specimens 5207 and 5208 were alumina-silicate based coatings which are proprietary to the PlasChem Corporation, St. Louis, Missouri. They exhibited severe degradation in solar absorptance of 0.152 and 0.102, respectively. The as received specimens appeared to have become contaminated by the tape used to wrap them for shipment.

The degradation exhibited by the zirconia specimens, numbers 5211 and 5212, were 0.095 and are indicative of a valid space-simulation test.

IV. ANOMALOUS DEGRADATION OF ZINC OXIDE AND S-13

A. Definition of the Problem

Reports (ref. 4, 5) that IITRI's S-13 thermal-control paint degrades severely in the infrared region and is not observable by post-exposure reflectance measurements, however immediate the measurement, prompted a series of experiments aimed at explaining this phenomenon.

Experiments were accordingly prepared which utilized the single-sample chamber constructed for a previous in situ reflectance experiment (ref. 6). This device, shown in Figure 1 and 2 consists of performing the in situ measurement through a quartz window with the evacuated specimen located in close proximity to the window. The measurement was then performed by placing the chamber such that the window is located at the sample port of the Beckman DK-2A spectrophotometer. Though subject to large errors in calculating absolute reflectance by this method, the device's precision was found to be sufficiently adequate for determining small reflectance changes in any spectral region covered by the DK-2A.

Previous work with the facility shown in Figures 1 and 2 made no attempt to measure the reflectance in the infrared, the device being incompatible with the sphere on the infrared reflectometer then in use. Furthermore, it was incorrectly assumed that an absence of differences in the visible region of the spectrum precluded differences in the near infrared for in situ reflectance measurements. It was therefore argued that post-exposure

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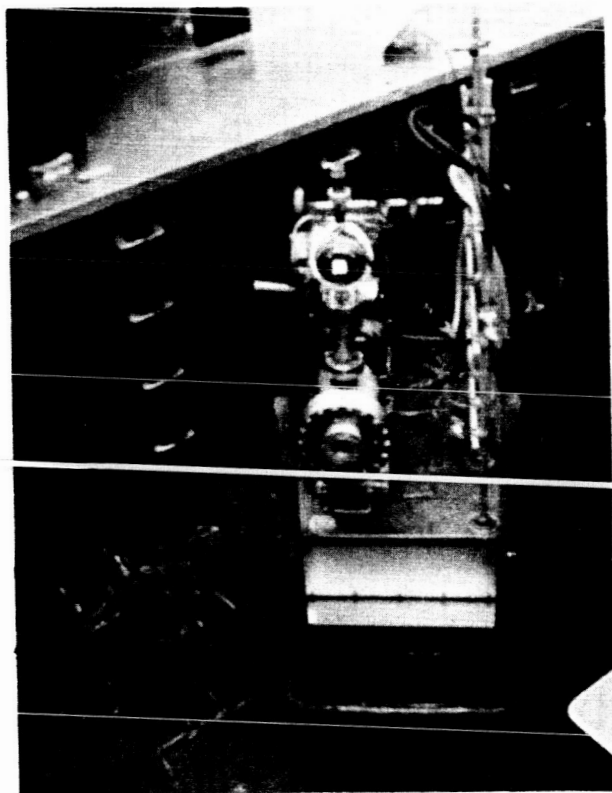


Figure 1

IN SITU REFLECTANCE/VACUUM FACILITY

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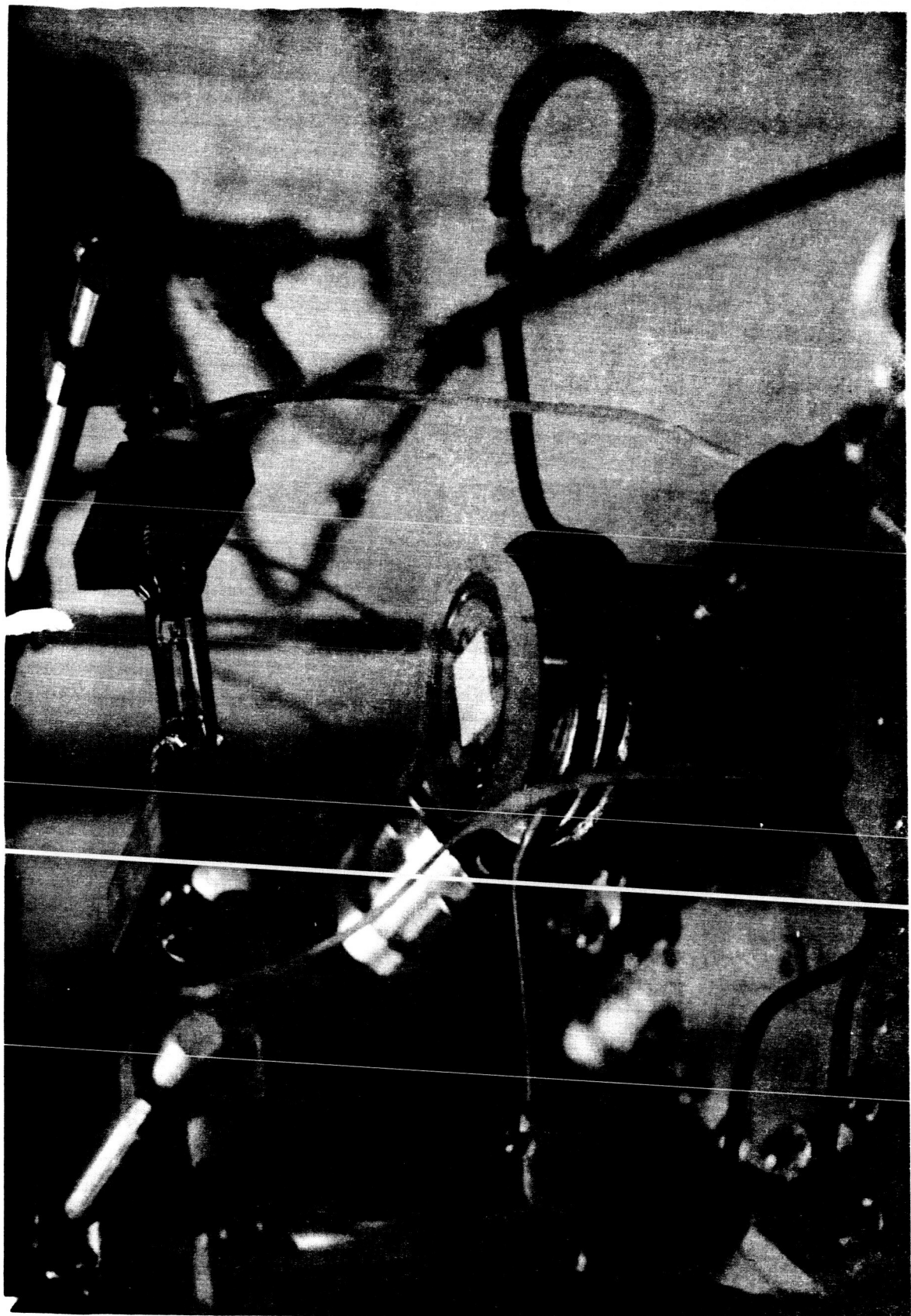


Figure 2

IN SITU REFLECTANCE/VACUUM FACILITY

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reflectance measurements were valid.

The first measurement was performed on a specimen of IITRI's S-13 paint, a zinc oxide-pigmented polydimethylsiloxane elastomer. The in situ reflectances before and after approximately 1200 ESH of ultraviolet irradiation are presented in Figure 3. These data confirmed the communications which are referenced earlier in this section (ref. 4,5). A reflectance decrease of 28% occurred at 2.05μ and the vacuum system was vented to the atmosphere. An almost instantaneous increase in reflectance occurred; a plot of reflectance at 2.05μ versus time after venting is presented in Figure 4. It will be seen that almost complete reflectance recovery occurred within two minutes.

A second specimen of S-13 was irradiated for only 15 minutes at a solar factor of 12X. The severe decrease in reflectance in the infrared, as manifested by the 11%-decrease at 2050μ , tends to indicate that a photodesorption phenomenon is involved in the observed decrease in reflectance when measured in vacuum. Indeed, two experiments, one with the N_2 -bleached SP500-powder specimen (see Table 6) and the other with an S-13 specimen irradiated for 3 ESH, have shown that re-evacuation of specimens results in a loss in reflectance corresponding to the initial reflectance decrease caused by the very short exposure to ultraviolet radiation.

Subsequent experiments were performed by irradiating for various times SP500 zinc oxide powder, Z93 (IITRI's zinc oxide-pigmented potassium silicate paint), unpigmented RTV-602 film,

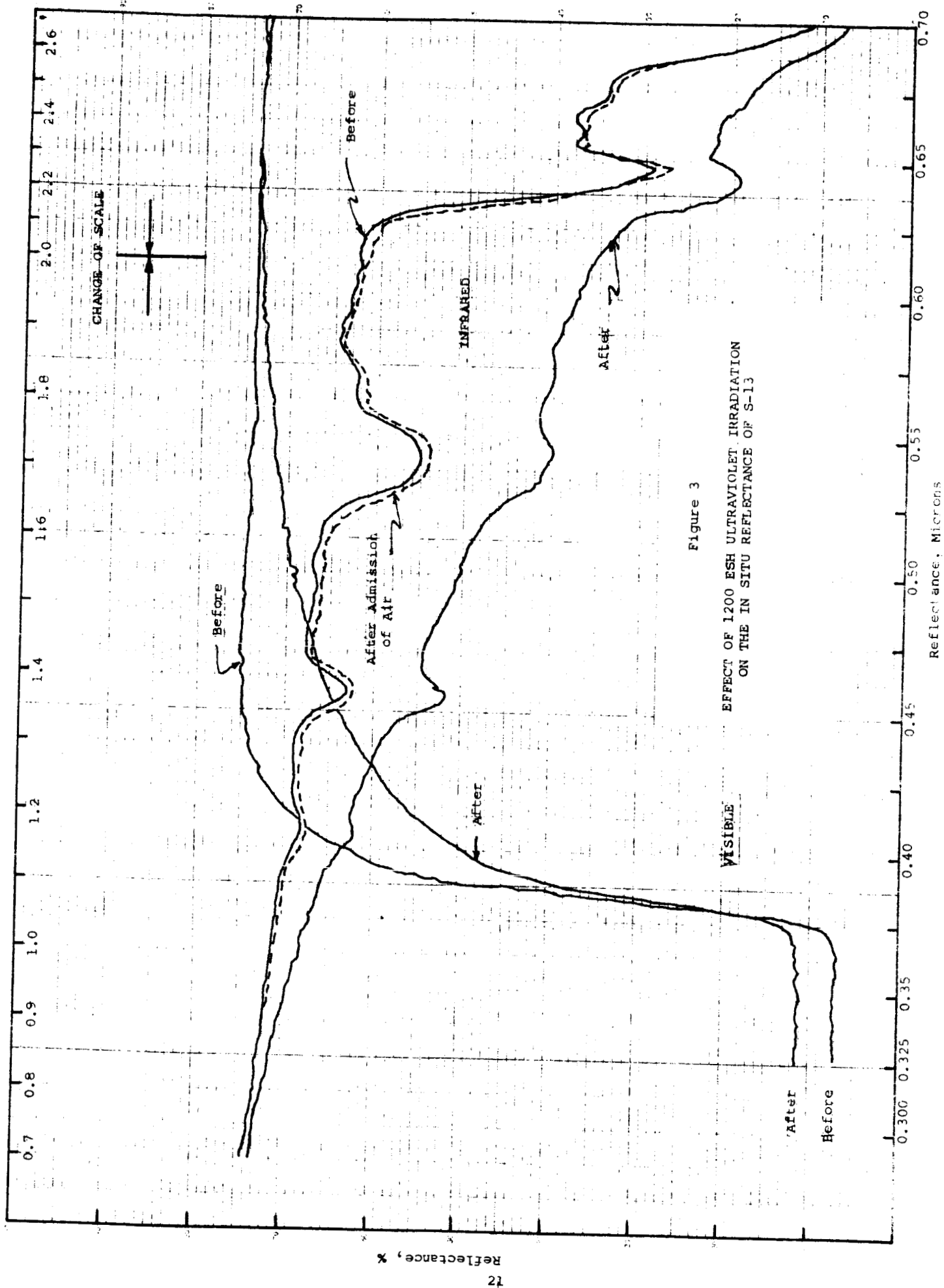


Figure 3
EFFECT OF 1200 ESH ULTRAVIOLET IRRADIATION
ON THE IN SITU REFLECTANCE OF S-13

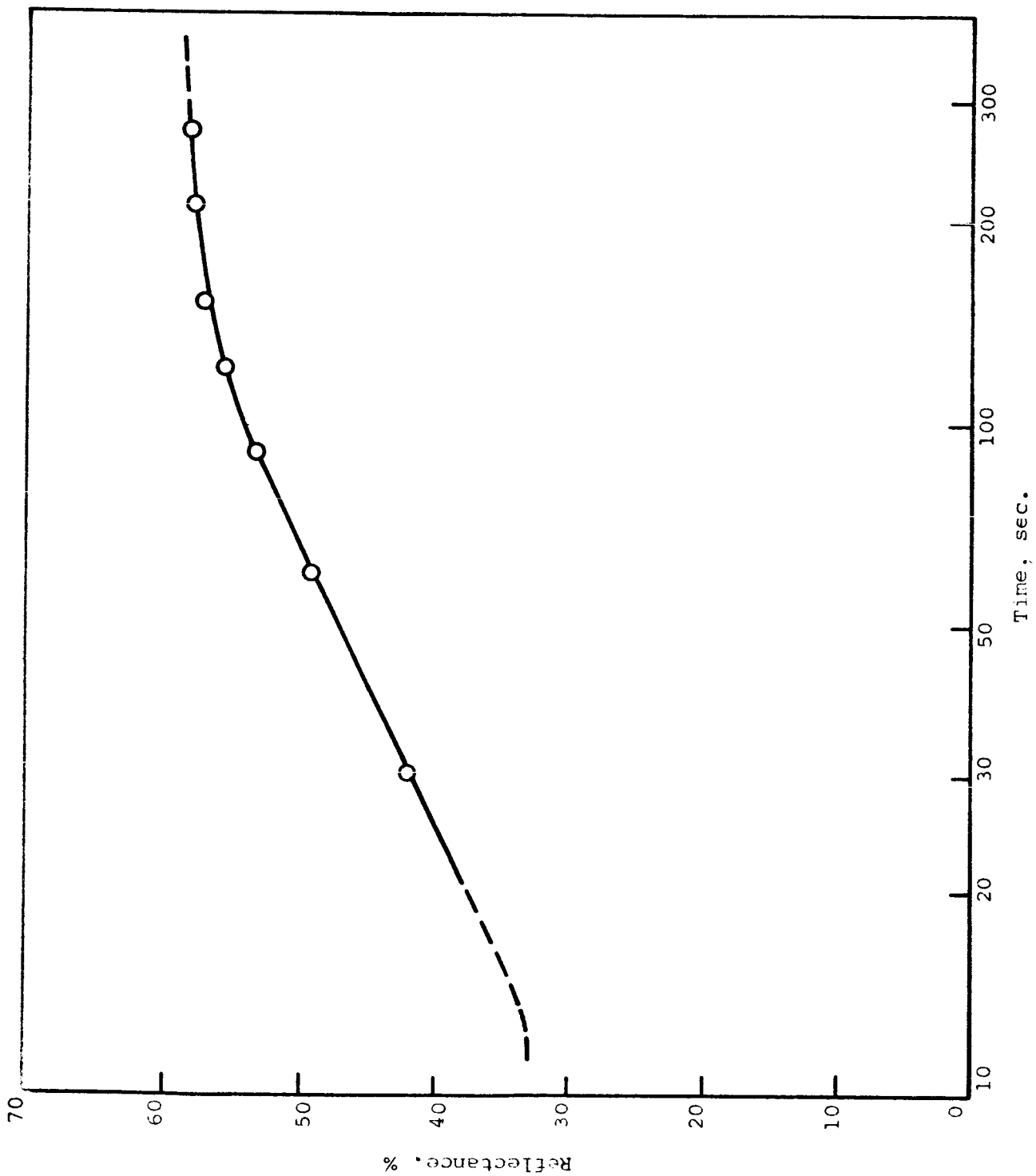


Figure 4

REFLECTANCE INCREASE AT 2.05μ
AS A FUNCTION OF TIME AFTER AIR INLET

a specimen of SP500 zinc oxide-pigmented Owens-Illinois type 650 glass resin, a second specimen of S-13 and a modified S-13 designated S-13G. Data resulting from these experiments are summarized in Table 6.

Table 6

IN SITU REFLECTANCE CHANGES FOR SPECIMENS IRRADIATED
WITH UV FOR VARIOUS EXPOSURES

Specimen	Exposure		Wavelength $m\mu$	$\Delta R\%$	Instantaneous Bleach
	Time	ESH			
SP500 ZnO	12 min	2½	2700	15	Air - Yes
	12 min	2½	2700	17	N ₂ - Yes
Z93	16 hr	200	2050	0.5	Air - No
RTV-602	16 hr	200	2050	0	N/A
ZnO/OI-650	46 hr	550	2050	19	Air - Yes
S-13	100 hr	1200	2050	28	Air - Yes
	15 min	3	2050	11	Air - Yes
S-13G	1 hr	12	2050	2	-
	2 hr	24	2050	2	Air - No
	120 hr	600	2050	0	N/A

The vacuum in situ reflectance spectra of SP500 zinc oxide before and after 2.5 ESH of ultraviolet irradiation is shown in Figure 5. A decrease in reflectance of 15% occurred at 2700 $m\mu$. Also shown in Figure 5 are the reflectance changes which occurred when (1) nitrogen was admitted to the system and (2) the irradiated specimen was subsequently re-evacuated. (The maximum change appeared to occur at greater than 2700 $m\mu$ for the powder specimen and

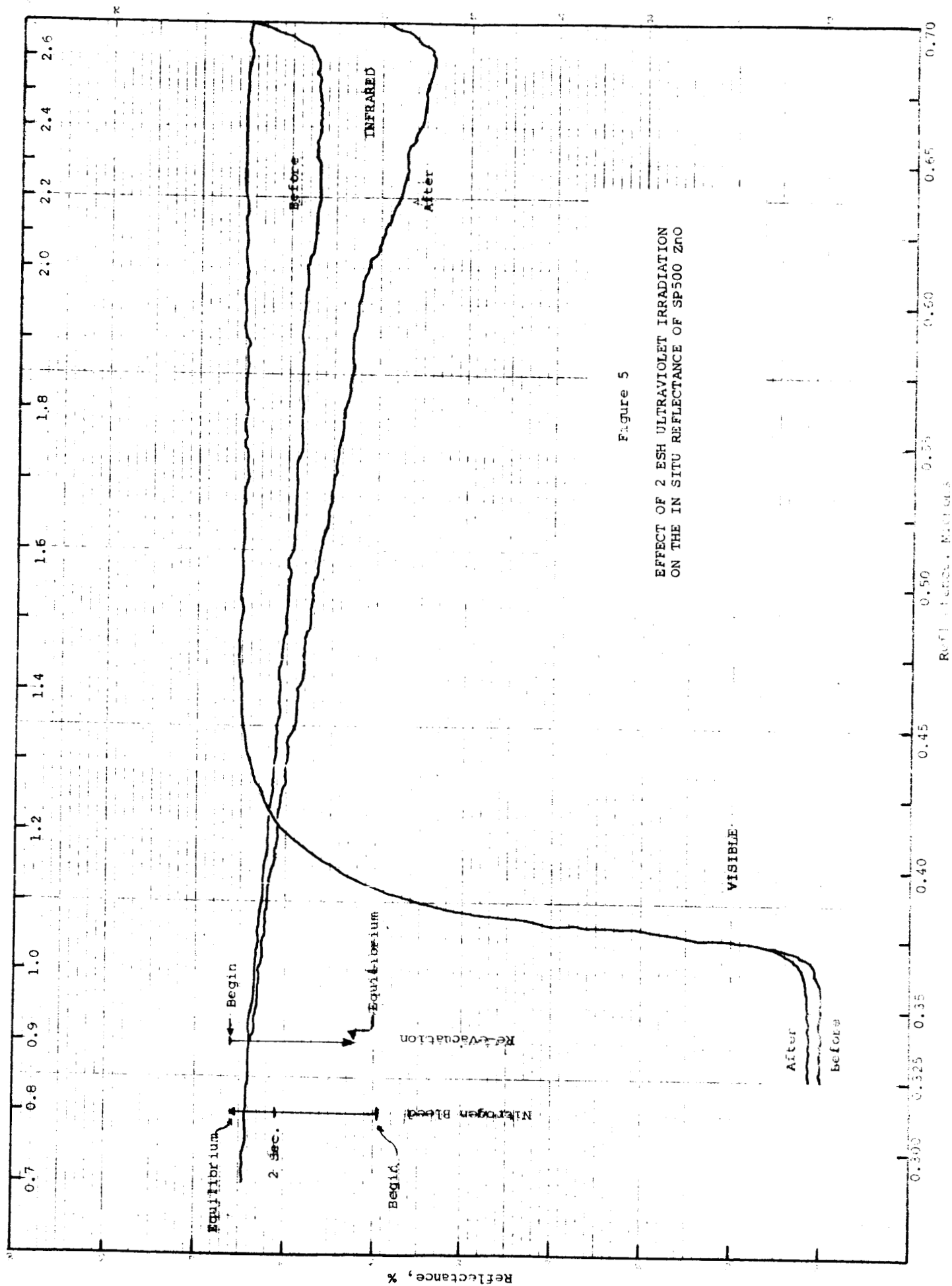


Figure 5
EFFECT OF 2 ESH ULTRAVIOLET IRRADIATION
ON THE IN SITU REFLECTANCE OF SP500 ZnO

this wavelength, the long-wavelength limit of the reflectometer, was therefore chosen to study the bleaching rate of the powder).

The Z93 specimen did not exhibit the anomalous infrared degradation observed for the pigment alone and for the S-13 specimens. No effect was observed when air was admitted to the vacuum system. The decrease in reflectance of 0.5% at 2050 $m\mu$ is thought to be due to experimental error. The spectra are presented in Figure 6. The reflectance increase is attributed to loss of water on irradiation in vacuum.

No changes in the in situ infrared reflectance of an unpigmented RTV-602 film were observed after 200 hours of irradiation. The possibility that the polydimethylsiloxane binder contributed to the observed degradation was thus eliminated.

A specimen of zinc oxide-pigmented Owens-Illinois type 650 glass resin paint, which has been previously observed to be the most stable white coating available (Reports IITRI-C6014-26 and IITRI-U6002-31), also exhibited the anomalous degradation in the infrared when the reflectance was measured in situ. The spectra are presented in Figure 7. It has been observed, however, that the effect is somewhat less than for the S-13 coatings.

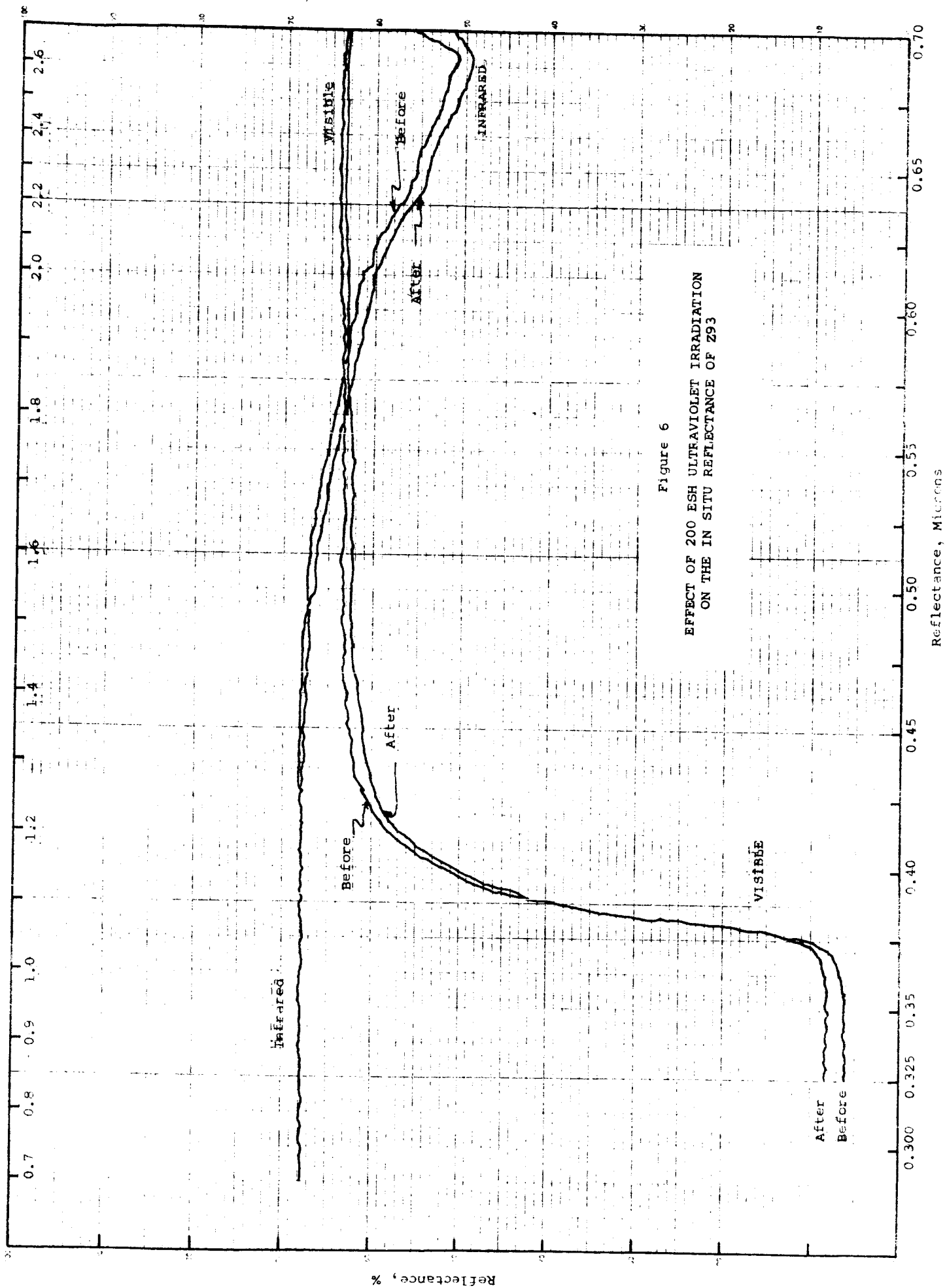


Figure 6
EFFECT OF 200 ESH ULTRAVIOLET IRRADIATION
ON THE IN SITU REFLECTANCE OF Z93

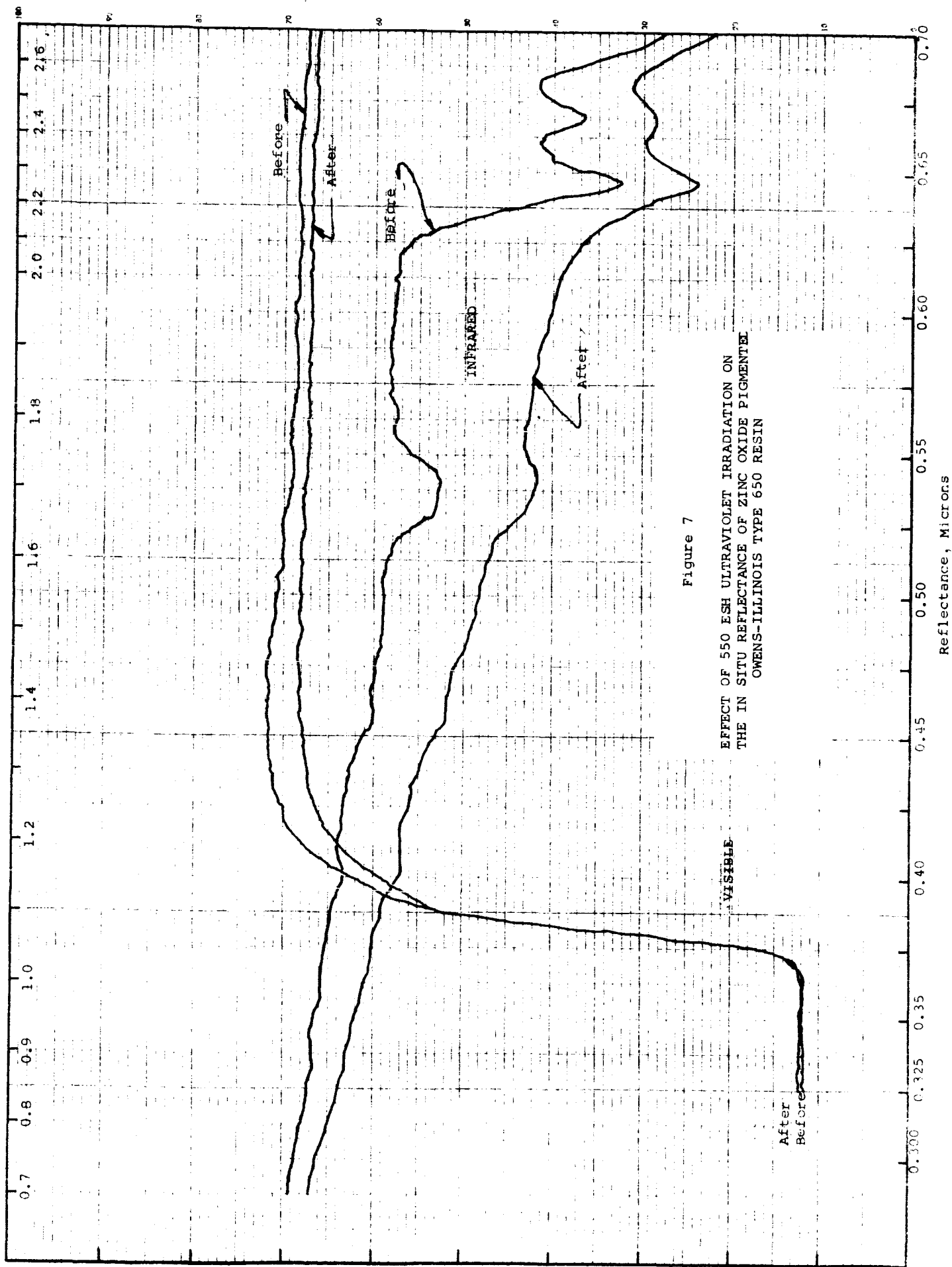


Figure 7

EFFECT OF 550 ESH ULTRAVIOLET IRRADIATION ON
THE IN SITU REFLECTANCE OF ZINC OXIDE PIGMENT IN
OWENS-ILLINOIS TYPE 650 RESIN

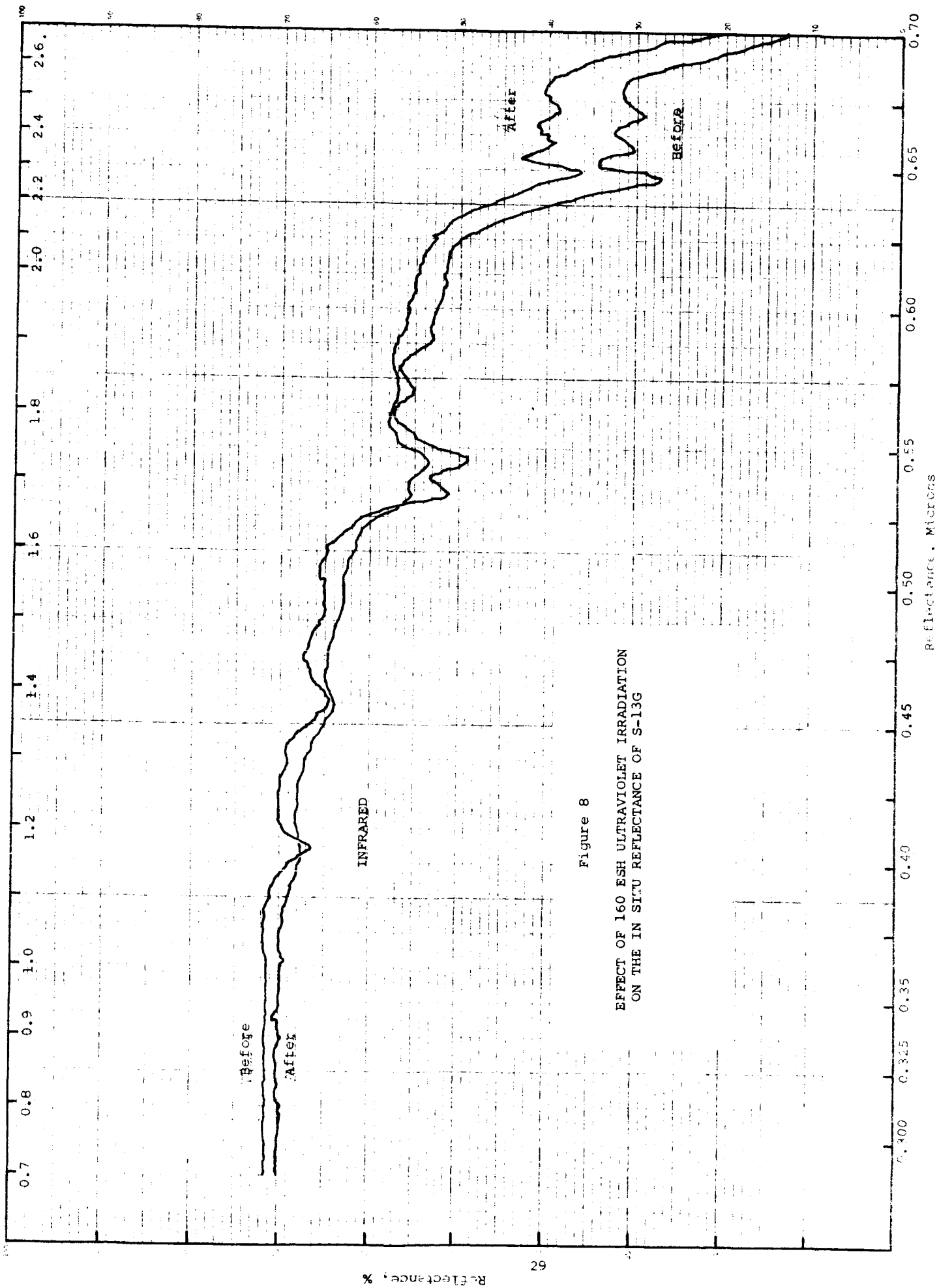
B. Analysis: Attempts to Solve the Problem

These observations led to the conclusion that the zinc oxide in Z93 paints is prevented from desorbing by either the formation of a "wetted" layer of potassium silicate or by the formation of the well-known but poorly characterized zinc ortho-silicate reaction product of zinc oxide and potassium silicate, both of which may act as a barrier to photodesorption processes. We accordingly initiated an experiment aimed at the surface treatment of zinc oxide in such a manner that photodesorption might be prevented.

The experiment involved the grinding of SP500 in PS7 potassium silicate followed by extraction procedures. The exact procedure is presented in Appendix I. An S-13 paint prepared from SP500 zinc oxide treated in this manner was designated S-13G. It was subsequently irradiated in vacuum for 1 hour. The reflectance decrease of only 2% at 2050 m μ , whether real or a result of experimental error, occurred in the first hour of irradiation. Additional irradiation for 1 hour did not further decrease the reflectance in the infrared and no change was noted when air was admitted to the irradiation chamber. The spectra of an S-13G specimen irradiated for 160 ESH is presented in Figure 8. The increase in infrared reflectance was surprising and may be due at least in part to loss of chemically bound water.

Subsequent tests of S-13G, S-13H (PS7-treated SP500 at 40% PVC) and S-13L (0.1% Li-doped ZnO at 30% PVC) were performed for 600 ESH (see Figures 9 through 11). The initial reflectance of S-13H was higher than that of S-13G; they both appeared to degrade

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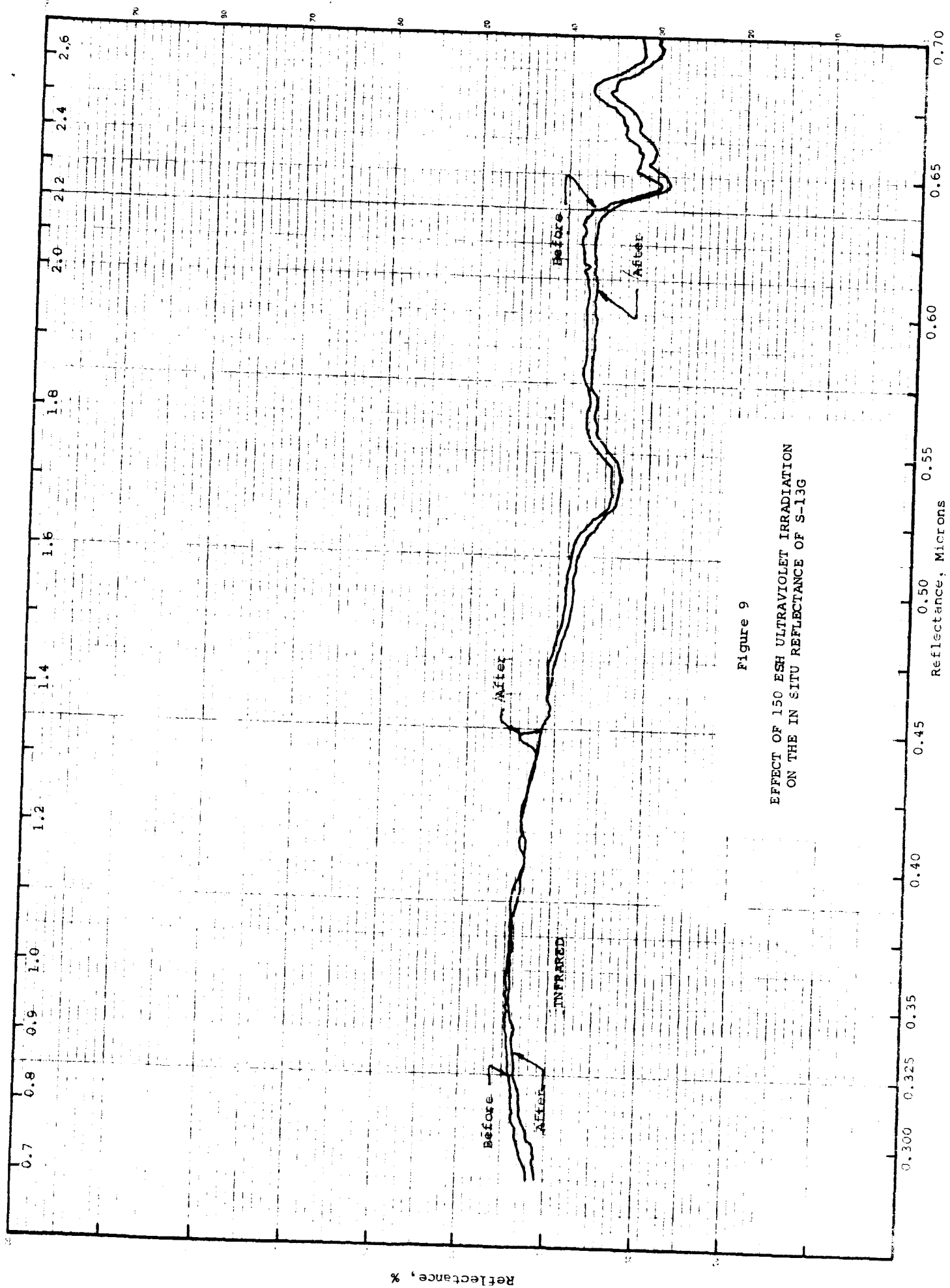


Figure 9
EFFECT OF 150 ESH ULTRAVIOLET IRRADIATION
ON THE IN SITU REFLECTANCE OF S-13G

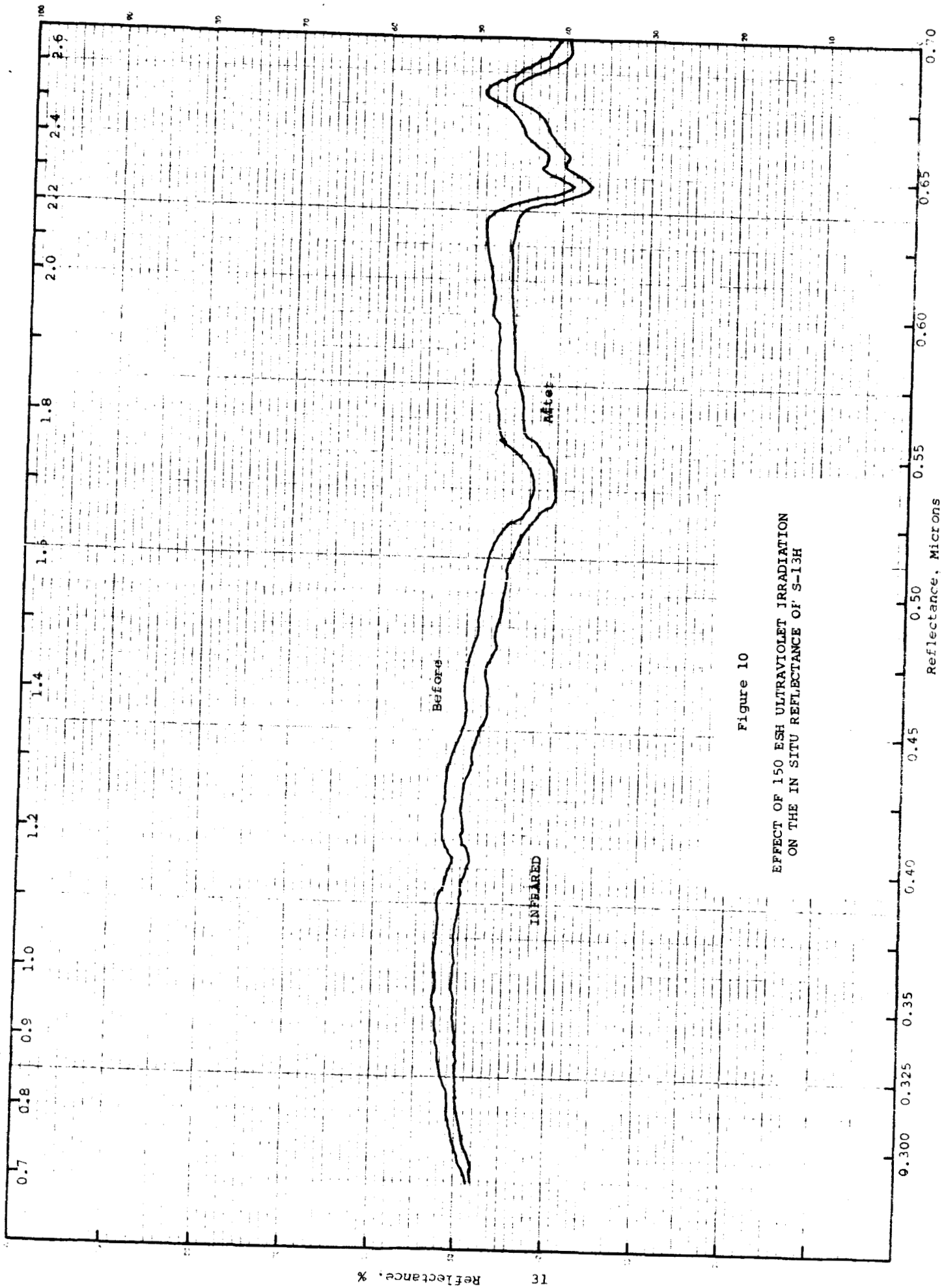


Figure 10

EFFECT OF 150 ESH ULTRAVIOLET IRRADIATION
ON THE IN SITU REFLECTANCE OF S-13H

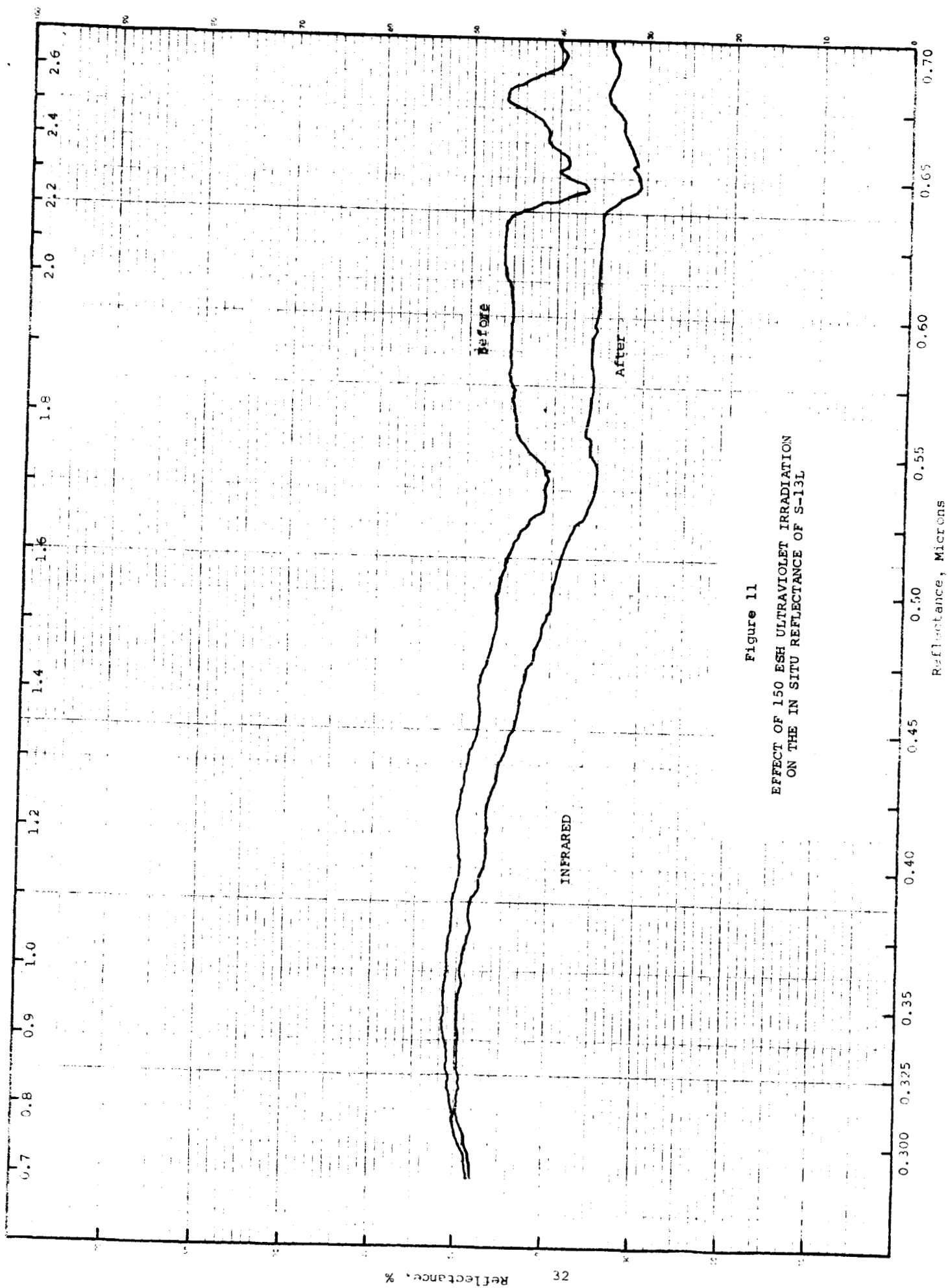


Figure 11
EFFECT OF 150 ESH ULTRAVIOLET IRRADIATION
ON THE IN SITU REFLECTANCE OF S-13L

about 2-3% at $2.05\ \mu$, however. It should be noted that the 600 ESH test was performed through a thicker window; thus transmission and scattering losses were increased, which accounts for the lower in situ reflectance presented in Figures 9-11. The degradation at $2.05\ \mu$ of 11% for S-13L specimen was disappointing and is in direct contrast to the observations of the pure Li-doped powder (ref. 7).

The constancy of the reflectance changes from 700 to $2700\ m\mu$ for Figures 9 to 11 is attributed in part to experimental error introduced by making these in situ reflectance measurements through a thicker window. Therefore, except for the S-13L specimen which exhibited a non-constant, increasing reflectance loss with wavelength, little or no change is believed to have occurred for either S-13G and S-13H in these tests.

A second pigment-treatment experiment involved the hydrolysis of mixed silanes on the surface of the zinc oxide in the belief that the mono- and polymolecular layers of water adsorbed on the particle surfaces would affect both the polymerization of the silane and "wetting" of the resultant polymer. The procedure ultimately used is presented in Appendix II.

A paint designated S-13K was prepared from the first silane-treated SP500 zinc oxide. It did not properly cure and turned black when heated in vacuum. These difficulties were attributed to the presence of residual chloride ion. A second pigment treatment involved greater care to remove chloride ion. However, the RTV-602-based S-13K paint prepared from this batch (Appendix II)

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also failed to cure; simulation tests were therefore not made on this paint. Additional studies of silane-treated SP500 are currently in progress.

C. Conclusions

It has thus been shown that the zinc oxide pigment is responsible for S-13's anomalous degradation in the infrared which is observed when reflectance is measured in vacuum. In our opinion, the difference in behavior between the potassium silicate-based Z93 and the methyl silicone-based S-13 lies in the protective nature of the silicate film. The potassium silicate solution is known to easily wet the zinc oxide surface. The methyl silicone polymer, on the other hand, does not wet the pigment particles and dispersion is affected only after grinding in a suitable ball mill.

The increased absorption of zinc oxide on irradiation in vacuum at wavelengths greater than 1 micron is probably the result of both (1) impurity bands more than 1 eV below the conduction band, and (2) free carrier absorption. The lower the negative surface charge due to diffusion of zinc to the surface with a corresponding increase in the density of hole traps below the surface, the more electrons may become available for free carrier absorption. This effect should be very sensitive to the oxygen partial pressure, as has been observed in these studies.

Additional studies relating to powdered zinc oxides were performed on a program for the Jet Propulsion Laboratory (ref. 7). Some additional conclusions of these studies are: (1) the effect could be induced in exposures of 1 ESH, or less, (2) the reflectance recovers to nearly its original value even after admitting pure nitrogen (the recovery rate is similar to that when air is

admitted); admission of organ produces no effect, and (3) a lithium-doped zinc oxide (0.1% Li) did not display the reflectance anomaly.

The potassium silicate-treatment of SP500 zinc oxide appears to have solved - at least in the preliminary tests outlined herein -- the infrared degradation problem exhibited by the S-13 thermal-control paint as observed by in situ reflectance measurements. The treatment is also expected to have a beneficial effect on the S-33 and Owens-Illinois type 650 coatings as well. Studies are currently being performed to adapt the silicate-treated SP500 zinc oxide to other silicone systems.

V. SIMULATION FACILITY WITH IN SITU REFLECTANCE CAPABILITY

The design of a multiple-sample ultraviolet-simulation chamber with in situ hemispherical-spectral-reflectance-measurement capabilities has been completed. This work was initiated because of the need for more definitive studies of the behavior of thermal-control materials in vacuum -- particularly the measurement of hemispherical reflectance in situ.

A schematic of the facility is presented in Figure 12. The integrating sphere is patterned after Edwards et al (ref. 8) as modified by Bevans (ref. 9) for the Beckman DK-2A. It will differ from one constructed earlier (ref. 10) by virtue of its evacuation and the changes necessitated by operation in vacuum. The facility possesses a 12-sample sample-exchange mechanism which permits the removal of any one of the 12 samples to the integrating sphere for measurement and the subsequent return to the sample table for continued irradiation.

A schematic of the sample table assembly and the sample-interchange mechanism is shown in Figure 13. The bottom drawing is a side view showing two cut-away samples in position. They are pressed to the liquid cooled sample table by the spring mechanism shown in the drawing. The samples are held by pins inserted into each. The entire sample-holding device can be rotated by a bellows-equipped indexing arm (not shown). The pressure between the cooling chamber and the samples is released by pressurizing the bellows (which are shown). A second bellows-equipped arm (not shown) moves the sample from the pin to the

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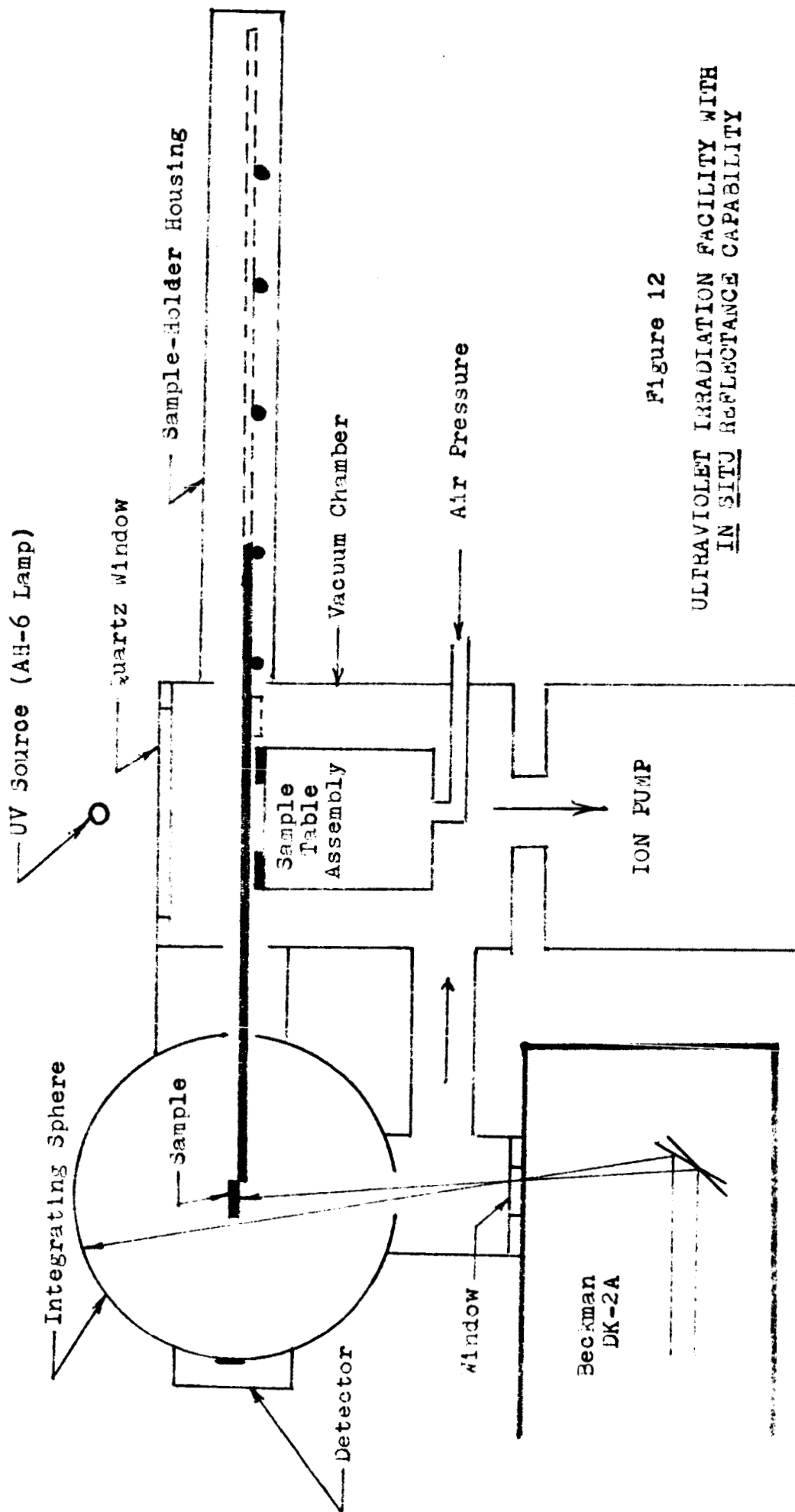


Figure 12

ULTRAVIOLET IRRADIATION FACILITY WITH
IN SITU REFLECTANCE CAPABILITY

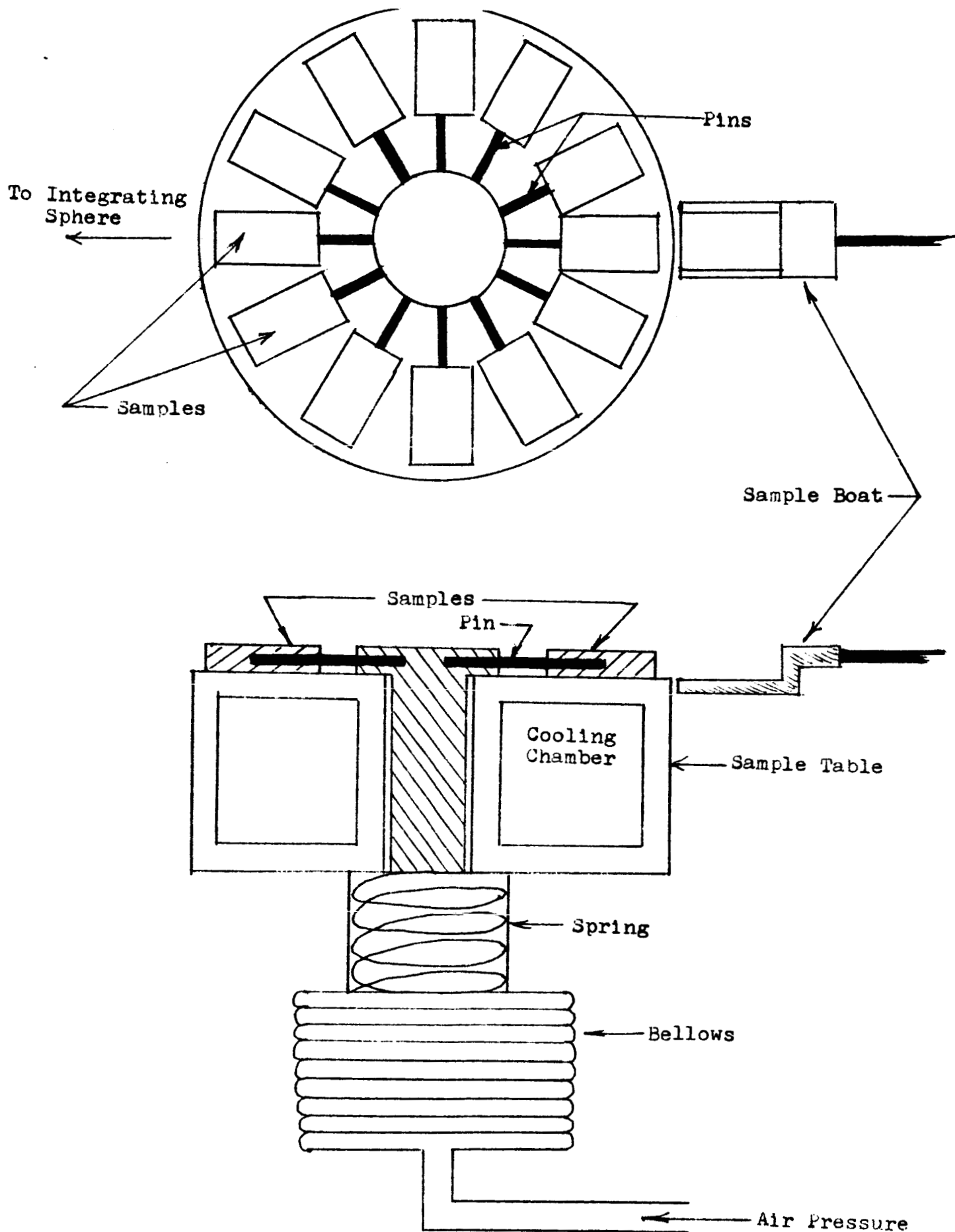


Figure 13

SAMPLE TABLE ASSEMBLY AND INTERCHANGE MECHANISM

sample boat which is subsequently run into the integrating sphere for measurement.

We are currently checking out the more than 100 engineering drawings and anticipate that machine work will commence within the next month. It is planned that the entire set of engineering drawings will be made available to NASA as a separate Technology Utilization Report.

VI. SILICONE PHOTOLYSIS

The new photolysis train has been constructed and will be attached to the Hitachi RMU-6D mass spectrometer during the month of March. The principle feature of the new train is the elimination of diffusion-pumping in favor of adsorption-pumping. This will result in a cleaner background spectra and should preclude the possibility of external contamination.

APPENDIX I

SILICATE-TREATED SP500 ZINC OXIDE

Approximately 600 grams of "as received" SP500 zinc oxide (New Jersey Zinc Company) are thoroughly mixed with 1200 grams of PS7 potassium silicate (Sylvannia) in a 2-quart capacity ball-mill jar. Approximately 20 cylindrical grinding stones, 1 in x 1/2 in diameter, are added to the mill and the slurry is ground at approximately 75% of critical speed for 45 minutes. The ball-jar is removed from the mill and the ground mixture is allowed to stand approximately 16 hours. The slurry is then re-ground for 10 min.

The ground slurry is transferred to a 3 liter beaker and diluted with 800 ml of distilled water. The mixture is thoroughly stirred and transferred to a large Buchner funnel and filtered at reduced pressure through a #597^{*} filter paper. The filter cake is washed with 3 liters of distilled water and pumped dry. The filter cake is removed from the funnel and spread on an aluminum foil tray. The contents are placed in a forced-air oven and dried for 16 hours at 100°C. The dried treated-pigment is then placed in a completely dry mill jar and dry ground with approximately 20 grinding stones for 15 min. The resultant treated-pigment is then re-heated for 1 hour 100°C.

The PS7-treated SP500 zinc oxide is then used to prepare the S-13G and S-13H thermal-control paints. The formulations are:

^{*} Schleicher and Schuell Analytical Filter Paper.

<u>Constituents</u>	<u>S-13G</u>	<u>S-13H</u>
PS7-Treated SP500 ZnO	240	374
RTV-602 silicone	100	100
SRC-05 catalyst	0.5	0.5
Toluene	184	215
<u>PVC</u>	<u>30%</u>	<u>40%</u>

APPENDIX II

SILANE-TREATED SP500 ZINC OXIDE

A mixture of 39 grams (0.3 moles) of dimethyldichlorosilane and 72 grams (0.48 moles) of methyltrichlorosilane are thoroughly mixed with 60 grams of SP500 zinc oxide in an otherwise empty 1/2-pint mill jar. An exothermic reaction occurs. Approximately 12 spherical grinding stones, nominally 1/2-in dia, are added and the contents are ground at approximately 75% of critical speed for 1/2-hour. (The exothermic reaction has been observed to cease after approximately 15 min of grinding.) The mill contents are then added to a 5% solution of sodium bicarbonate (NaHCO_3) with agitation, and the mixture is mechanically stirred for 2 hours. It is then filtered through a fritted Buchner-type funnel. The filter cake is washed with approximately 3 liters of distilled water until a neutral (to pH paper) filtrate is obtained. The filter cake is placed in a beaker with 1 liter of distilled water and mechanically stirred for approximately 3 hours. The mixture is again filtered through the fritted funnel and pumped to dryness. The filter cake is spread in an aluminum-foil tray and dried for approximately 18 hr at 100°C in a forced-air oven. The dried silane-treated pigment is then dry milled for 15 min in a completely dry mill jar (with about 12 grinding stones). The ground pigment is then returned to the oven and dried for 1 hour at 100°C. The silane-treated pigment is then used to prepare an S-13K formulation (which has not cured to date). The formulation is:

<u>Constituents</u>	<u>Pts/wt</u>
Silane-treated SP500 ZnO	240
RTV-602 silicone	100
SRC-05 catalyst	0.5
Toluene	184

NOTE: THE INITIAL HANDLING AND BICARBONATE DILUTION SHOULD
BE PERFORMED IN A HOOD

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